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20. Abstract (Contd)

Traces of moisture in LiCl-KCl melts were found to exert profound influences upon certain electrode processes. In the reduction of chromate ion, in the absence of divalent ions moisture produces a prewave limited by water concentration, occurring before the main reduction step. This wave, while proportional to water content is not simply diffusion controlled but is partially kinetically controlled. In the electro reduction of chromium(III) to chromium(II), the presence of traces of moisture result first in a reversible hydrolysis step followed by irreversible polymerization reactions finally yielding insoluble products.

Molybdate in the presence of zinc chloride in LiCl-KCl melts gives $\text{Li}_2\text{ZnMo}_2\text{O}_8$, which can be regarded as a compound of two MoO_4^{3-} ions packed into a lattice with Li^+ and Zn^{2+} .

Antimony doped tin oxide is a useful anode material in LiCl-KCl melts. Eu(III)/Eu(II) and $\text{iron(III)/iron(II)}$ show essentially reversible behavior whereas copper(II)-copper(I) and Pt(IV)/Pt(II) show abnormalities attributed to adsorption of the reduced form via chloride bridges.

Zirconia based solid electrolytes of various compositions have been tested as membranes for electrodes specific to oxide ions. Y_2O_3 - stabilized zirconia proved to be the best electrolyte, responding almost in accordance with theory to oxide ion activity.

ELECTROCHEMISTRY OF FUSED SALTS

FINAL REPORT

H. A. Laitinen

March 1, 1975 - February 28, 1979

U. S. Army Research Office

DAHCO4-75-G-70092

Department of Chemistry
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Foreword

This report includes a summarizing description of research projects performed during the period March 1, 1975 - February 28, 1979 together with references to the published literature. For the final project on the development of an oxide ion electrode for KCl-LiCl eutectic melts, the manuscript of a report by Isaac Hodara is included as an appendix. Although this work was presented at the Honolulu ACS meeting in April, 1979, it remains incomplete and the research has been discontinued owing to lack of financial support.

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I. On the Mechanism of Chromate Reduction in LiCl-KCl Melts(1).

Previous studies in our laboratory had indicated that chromate undergoes a single 3-electron reduction process which is profoundly affected by the presence of various divalent ions. During the present phase of the research, the fundamental reaction in the absence of divalent ions was more thoroughly investigated. It was found that Li_3CrO_4 can be prepared as a relatively stable compound, which however slowly undergoes a disproportionation reaction to yield solid LiCrO_2 and chromate ion. In the presence of zinc(II), magnesium(II), and nickel(II) ions the composition of the product varies with the nature of the cation. Compositions similar to those produced electrochemically in the presence of these divalent cation ions can also be made by direct chemical reaction of Li_3CrO_4 . It is therefore believed that the electrochemical process involves the one-electron intermediate which then undergoes a secondary disproportionation reaction. In the presence of calcium(II) and cadmium(II), the disproportionation yields LiCrO_2 and chromate ion.

In a separate study (2) the electrode potential of the chromate(VI)- solid lithium chromate(V) system in molten LiCl-KCl eutectic was investigated. This system was found to be electrochemically reversible, and the equilibrium constant of the disproportionation reaction of solid Li_3CrO_4 was evaluated.

II. Some Effects of moisture in LiCl-KCl Melts.

A method of introducing controlled amounts of moisture into molten eutectic salts was developed. Argon with a known partial^{pressure} of water vapor was prepared by bubbling the argon through mixtures of sulfuric acid and water of known composition at constant temperature. The moist argon was bubbled through the melt until equilibrium was established, generally in 30 min or less. The use of existing data on the solubility of water vapor in LiCl-KCl melts, provides a calibration suitable for

analytical methods such as steady state voltammetry. Moisture introduced in this manner could be removed by bubbling dry argon through the melt. However, by using HCl gas the removal of moisture was much more rapid and complete. As an example, the moisture content of a sample of LiCl-KCl eutectic was determined to be 4.5 mM, which could be decreased to less than 0.1 mM in 15 min of bubbling by dry HCl gas. Several cycles of moisture addition and removal did not appreciably degrade the shape of residual current curves.

A. Effect of moisture on chromate reduction(3).

Under highly dehydrated conditions, chromate shows a single 3-electron reduction step in molten LiCl-KCl eutectic. This reduction occurs at -1.18 V vs a platinum reference electrode. In the presence of a trace of moisture, two reduction steps are observed, the first at -0.6 V and the second at -1.18 V (3). Coulometric experiments revealed that 3-electrons and 2 water molecules are consumed per chromate ion and that LiCrO_2 is formed as an insoluble product at the first reduction step. Chronopotentiometric experiments indicated that, while the first reduction step is limited by the water content of the melt, it is not completely controlled by diffusion of H_2O . The first reduction step is partially controlled by reaction kinetics and partly by diffusion of water. The second step is controlled by diffusion of chromate.

In principle, the first reduction step could serve as the basis of a method for the determination of moisture in melts. The wave height is proportional to moisture concentration when the latter is less than the chromate concentration. However, the method would require calibration and careful temperature control because of the complex mechanism.

B. Effect of moisture on the chromium(III)-chromium(II) electrode reaction(4).

Using cyclic voltammetry at a glassy carbon indicator electrode, the hydrolysis of chromium(III) in molten LiCl-KCl eutectic has been studied by varying the ratio

of H_2O to HCl vapor pressure in equilibrium with the melt. In a dry melt the charge transfer reaction between chromium(III) and chromium(II) is rapid and reversible. There is, however, evidence of a slow chemical reaction of the chromium(II) following the charge transfer step. This is believed to be the dissociation of the octahedral hexachlorochromium(II) complex to the tetrahedral tetrachlorochromium (II), for which there is spectroscopic evidence.

In the presence of traces of moisture, the charge transfer reaction initially remains reversible, but gradually the concentration of electroactive species decreases without the appearance of a precipitate. It is believed that the first step of hydrolysis yields pentachlorohydroxy chromium(III) complex in a reversible hydrolysis reaction. This species undergoes a reversible charge transfer complex to the corresponding chromium(II) complex. Subsequent polymerization reactions form bridged species through irreversible reactions, first forming soluble species and finally an insoluble oxychloride of chromium(III). Once the bridging reaction has occurred, it no longer can be reversed by flushing out the moisture with dry HCl gas. Likewise, the soluble bridged polymers do not undergo reversible charge transfer reactions to form chromium(II). As a result, the concentration of electroactive species gradually decreases even before an insoluble phase is produced.

III. Electrochemical Reduction of Molybdate in the Presence of Zinc Chloride in Molten LiCl-KCl Eutectic (5).

Past work in our laboratories had shown that the electrochemical reduction of chromate in the presence of chloride yields a deposit of the composition $LiZn_2CrO_4$. Also previous studies of the reduction of molybdate showed the formation of a product $Li_5Mo_2O_8$, which can be regarded as a double compound of Li_2MoO_4 and Li_3MoO_4 incorporated into a single crystal lattice.

The chronopotentiometry of molybdate in the presence of zinc chloride showed two reduction steps occurring at -1.5 and -1.75 V vs the Pt(II)/Pt reference electrode, respectively. An increase of molybdate concentration causes a decrease of the first reduction step, which is attributed to the reduction of free zinc chloride. Addition of molybdate causes a decrease in zinc(II) concentration due to the formation of sparingly dissociated ZnMoO_4 . The equilibrium constant for the formation of ZnMoO_4 was calculated.

Analysis of the reduction product yielded an empirical formula $\text{Li}_4\text{ZnMo}_2\text{O}_8$, which would involve the reduction of MoO_4^{2-} to MoO_4^{3-} , which is then incorporated into a crystal lattice with Li^+ and Zn^{2+} in the appropriate ratio.

IV. Some Redox Reactions on Semiconducting Tin Oxide Electrodes in Molten LiCl-KCl Eutectic (6).

Antimony doped tin oxide, in the form of thin layers on glass substrates, is of interest as a possible electrode material, especially ^{for anodes,} in molten chlorides. The first experiments consisted of cyclic voltammetric scanning experiments in pure LiCl-KCl to study the surface conditioning of such electrodes. It was found that under repeated scanning, a relatively high background current was observed, especially at anodic potentials in the first scan. The current gradually decreased with repeated scanning, reaching a stable and reproducible condition after about the fifth scan. At this point, the background current at SnO_2 electrodes was several-fold smaller than at glassy carbon electrodes, especially in the anodic region. The conditioning process is interpreted as due to replacement of surface oxide groups by chloride ions, the oxide ions being anodically oxidized. After several cycles, all surface oxide sites are converted to chloride sites.

The conditioned tin oxide electrodes were used to study the electrode reactions of several redox couples using cyclic voltammetry. The charge transfer reactions

of the Eu(III)/Eu(II) and chromium(III)/chromium(II) couples were found to be reversible. The chromium(III) reaction was complicated slightly by hydrolysis due to traces of moisture. Unfortunately, measurements in a melt saturated with HCl to prevent hydrolysis could not be carried out at tin oxide electrodes because the tin oxide film is chemically dissolved by melt in the presence of HCl.

The oxidation of copper(I) and iron(II) affords an interesting comparison, because the standard potentials of the two oxidation reactions are quite close (0.061 V and 0.086 V respectively. Both are close to the anodic limit imposed by chlorine evolution (about 0.2 V). The iron(II)-iron(III) system shows the expected behavior, complicated only by the large background current for the anodic process. On the other hand, the anodic process for copper(I) does not show the expected anodic peak, whereas the cathodic peak is close to the expected result. It is believed that the difference between the copper and iron systems arises from the fact that copper(I) in solution is not coordinatively saturated, and therefore undergoes specific adsorption through bridging chloride ions. With iron(III), as well as with Eu(III) and chromium(III), no abnormal effects due to adsorption were observed. For iron(II) which has tetrahedral coordination, specific adsorption does not seem to occur. On the other hand Pt(II), which forms the square-planar complex PtCl_4^{2-} , might be expected to show specific adsorption. Such a behavior was indeed observed, in that no oxidation peak was observed for the oxidation Pt(II) to Pt(IV) but a reduction peak on the return scan was found. Finally, it was observed that, in contrast with aqueous solutions at room temperature, no rectification effects due to slowness of electron transfer through the space charge region could be observed, even under anodic conditions. It is concluded that in the high temperature melt system the observed carrier concentration becomes larger than at room temperature and electron tunneling through the space charge region is therefore favored.

V. Development of an Oxide Ion Electrode for KCl-LiCl Melts.

Oxide ion activity measurements based upon oxygen electrode or metal-metal oxide electrodes are of limited utility in chloride melts. Oxide-ion conductive membranes, especially CaO or Y_2O_3 stabilized zirconia or Y_2O_3 stabilized thoria have found several applications in high temperature systems. Limitations of these systems are discussed. The present work deals with an evaluation of zirconia and thoria tubes of various Y_2O_3 and CaO contents for membrane cell measurements in LiCl-KCl melts, using various reference electrodes. While both 8 wt/o Y_2O_3 stabilized zirconia and 8 wt/o Y_2O_3 stabilized thoria gave almost theoretical Nernstian responses, the former is preferred due to lower cost and greater mechanical strength. CaO stabilized zirconia was unsatisfactory. Slowness of response is a major restriction to practical applications. Some approaches to possible improvements are discussed.

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Appendix I

DEVELOPMENT OF AN OXIDE ION ELECTRODE FOR
KCl-LiCl EUTECTIC MELTS

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January, 1978

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Introduction

The development of an electrode specific to oxide ions for use in molten salts is of importance to the understanding of the electrochemistry of acid-base reactions in molten salts and to research and development efforts being made in many fields such as battery programs, nuclear reactors and electrolytic production of metals.

The objective of the present study is to develop a specific electrode for the determination of oxide ion activity in melts. This work is related to the ERDA project on the development of high temperature, high energy Li-S batteries (1).

The survey of the literature showed that, although many attempts were made in the past to develop such an electrode, none can be considered as having reached a reasonable state of usability and reliability even at laboratory scale.

In an early study of the electrochemistry of metal-metal oxide couples, Laitinen and Bhatia (2) showed that most metal oxides behaved either irreversibly or had excessive solubilities to be of value as oxide ion electrodes.

Wrench and Inman (3) used gold and platinum electrodes to follow changes in oxide ion activities in LiCl-KCl melts. They found that, the change in potential did not follow Nernst's equation for a reversible oxide electrode and that the electrodes were sensitive to the oxygen partial pressure above the melt.

Combes, Vedel and Tremillon (4) used a stabilized-zirconia solid electrolyte membrane as an electrode specific to oxide ions. With a 12 to 14% CaO stabilized zirconia electrode they obtained titration curves for oxide ions in NaCl-KCl melts at 720 to 800°C. For titrants, they used coulometrically generated

Cu^+ or Ni^{++} ions. A good Nernstian response to changes in oxide ion activity was obtained in basic solutions (excess oxide). In acid solutions, however, deviations from Nernstian behavior were observed, which were attributed to the contribution of chloride to ionic conductivity.

In a potentiometric study, Zambonin (5) observed that gold and platinum foil electrodes, when immersed in nitrate melts under oxygen pressure, behave as a superoxide electrode in the absence of water ($\text{O}_2 + \text{e}^- \rightarrow \text{O}_2^-$), while in the presence of excess water, an hydroxide electrode is obtained ($\text{O}_2 + 2 \text{H}_2\text{O} + 4\text{e}^- \rightleftharpoons 4\text{OH}^-$).

Flinn and Stern (6) also used CaO or Y_2O_3 stabilized zirconia with air or oxygen as reference gas to measure O^- , O_2^- , $\text{O}_2^{\cdot -}$ activities in nitrate melts, but could not obtain reproducible results. They assumed the reason to be due to the low working temperature slowing the rate of attainment of a reversible oxygen potential. Comparing the zirconia electrode potentials with those measured with a platinum wire electrode they were able to show that, the zirconia electrode responds to changes in oxide ion activities only, while the platinum electrode responds to changes in peroxide and superoxide ion activities as well, in oxygen saturated melts.

Recently, Combes, Vedel and Tremillon (7) demonstrated the use of CaO -stabilized zirconia electrodes to measure metal oxide solubilities, and Lysy and Combes (8) reported equilibrium constants for the $\text{OH}^-/\text{H}_2\text{O}$ and $\text{H}_2\text{O}/\text{HCl}$ reactions. As oxide reference in the zirconia tube an intimate mixture of Ni/NiO powder was used.

The use of various forms of stabilized zirconia or thoria as solid membranes in concentration cell type measurements have been known for a long time. A comprehensive review on the subject by Goto and Pluschkell (9) can be found in the

literature. These type of electrodes are commonly used for investigations in metallurgy, fuel cell research and glass and high temperature chemistry.

Recently, a sensor for remote monitoring of oxygen concentrations in which an internal reference electrode and an identical sensing electrode are coupled has been described (10). The internal oxygen reference pressure is generated by initially pumping out all the oxygen electrochemically, and then pumping it back into the cell until the oxygen partial pressures are equalized inside and out of the sensing electrode.

Uses of CaO stabilized zirconia membrane electrodes for measuring oxide ion activities in KCl and in CsCl melts are also found in the literature (11).

A Y_2O_3 stabilized thoria electrode for monitoring the oxygen level in liquid sodium for use in fast breeder reactors has been developed at the Argonne National Laboratories (12) jointly with the Westinghouse Nuclear Instrumentation and Control Department (13). It is shown that these electrodes with reference concentrations of oxygen flowing inside the electrolyte tubes, are extremely sensitive to changes in oxide ion activity in liquid sodium (ppm. range) and are fast and reliable.

In the present work, zirconia and thoria tubes of various Y_2O_3 and CaO contents were evaluated for application in KCl-LiCl melts. As reference, simple Ni/NiCl₂ electrodes sealed in ordinary 7740 pyrex glass tubes and oxygen or air in contact with platinum or gold surfaces were used. Generally, good Nernstian response was observed with Y_2O_3 stabilized zirconia or thoria tubes.

A solid electrolyte to be used as membrane electrode for the measurement of oxide ion activity, must have the following properties:

- imperviousness to the melt,
- selective to oxide ion transport,
- mainly ionic conductance,

- reasonably low electrical resistance,
- resistance to thermal shocks,
- resistance to chemical attack.

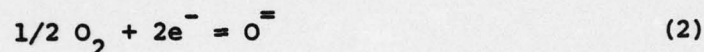
Theory

The State of Oxygen in KCl-LiCl Melts

The basis of the acid-base concept in molten salts, lies in the nature of the oxide ion which reacts with acidic species: (14-16)



In this equilibrium, the oxygen half-reaction may be represented as :



with the corresponding Nernst equation:

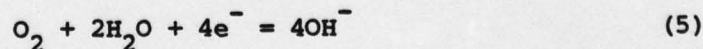
$$E = E_{O_2/O^{2-}}^0 + \frac{RT}{2F} \ln \frac{P_{O_2}^{1/2}}{[O^{2-}]} \quad (3)$$

The verification of the existence of the simple oxygen-oxide couple is complicated due to the extreme reactivity of the oxide ion. It will react with the walls of the vessel and parts of the experimental system, and almost with any metal, including platinum.

In the presence of moisture the reactions are even more complex, water behaving as an oxo-acid (acceptor of oxide) to produce hydroxyl ions:



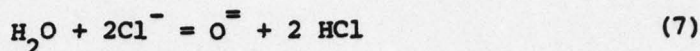
in which case the electrode will behave as a hydroxyl electrode:



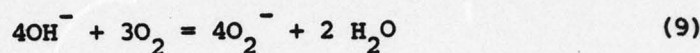
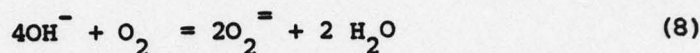
with

$$E = E_{O_2, H_2O/OH^-}^0 + \frac{RT}{4F} \ln \frac{P_{O_2} \cdot [H_2O]^2}{[OH^-]^4} \quad (6)$$

In acidic solutions, water behaves as a base to produce oxide ion (oxide donor):



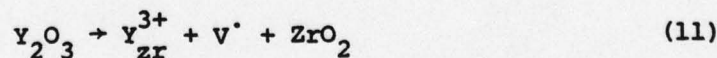
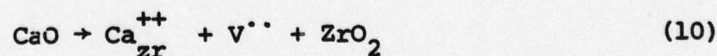
In the presence of oxygen, the occurrence of the following reactions should also be considered:



Solid Electrolytes as Membranes for Oxygen Concentration Cells.

In certain concentration ranges, solid solutions of zirconia with calcia, magnesia or yttria are cubic. These are called stabilized because the additives decrease the rate of phase transformation.

Stabilized zirconia electrolytes are ideally suited to serve as a specific medium for the transport of oxide ions, because solutions with 10 to 15 mole % of calcia or yttria provide enough oxygen vacancies for the oxide ions to migrate at a reasonable rate from one side of the membrane to the other. The so called oxygen vacancies are formed in order to accomodate for the valence difference of the cations:



$\text{Ca}_{\text{Zr}}^{++}$ or $\text{Y}_{\text{Zr}}^{+++}$ are a Ca^{2+} or Y^{3+} ion replacing a Zr^{4+} ion in the cubic ZrO_2 lattice, and $\text{V}^{\cdot\cdot}$ or V^{\cdot} show the charge vacancy formed to maintain electrical neutrality.

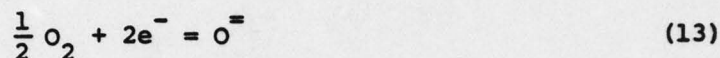
These vacancies provide an easy path for oxide ions to migrate within the lattice, accounting thus for the high ionic conductivity observed in these solutions (17).

An oxygen concentration cell built with a solid electrolyte membrane consists of two electrode compartments, each at different oxygen pressure, separated by the

solid electrolyte. In such a cell the membrane electrode responds to the ratio of oxygen partial pressure, or oxide ion activity on both sides of the membrane in a manner similar to the response of a glass electrode to changes in the ratio of hydrogen ion activity (18). The electrode potential response is of the form:

$$E = \frac{RT}{2F} \ln \frac{a_{O_2}}{a_{O^{2-}}} \quad (12)$$

for a half-cell reaction:



in opposing directions at the two sides of the membrane.

Apparatus

The Reactor

The molten salt reactor is constructed from 65 mm O.D. heavy wall pyrex tubing to fit the opening of a vertical furnace. The lower end of the tube is round bottomed while the upper end is terminated with a flat O-ring joint (Lab. Glass). A reactor top equipped with a similar joint is used to hermetically close the reactor. A McCarter type clamp holds the joints tightly together. Threaded adaptor tubes (Ace glass) sealed on the reactor top provide the necessary openings for the insertion of electrodes and inlet and outlet gas tubes.

Vacuum tight teflon bushings fitted with neoprene O-rings are used to hold the electrodes in place. Water at room temperature is circulated in a copper collar placed below the reactor top to prevent overheating of the openings, teflon bushings and O-rings.

A non-porous alumina crucible (Degussit Al-24) placed at the bottom of the reactor serves as container for the melt. The crucible is further protected by placing it into a pyrex beaker.

The reactor is connected to vacuum and argon lines through all glass connections.

A vertical furnace with resistance heating controls the temperature independently at the low, middle and top regions of the reactor.

The Vacuum Manifold

A rotary pump supplies the vacuum (10^{-2} torr) to the vacuum line containing two acetone-dry ice traps to collect water vapor. A mercury manometer indicates the pressure.

The Argon Line

99.5% pure argon is further purified by passing the gas through a purification train containing, in the given order, a column of anhydrous, copper turnings at 350°C, another anhydrous column and finally ascarite.

The manifold permits either vacuum suction or argon flushing of the reactor.

Supply of Other Gases

Provisions are made for passing cylinder hydrogen chloride gas through an anhydrous column to supply dry hydrogen chloride gas. In another line, parallel to the main line, argon gas can be saturated either with water or water-hydrogen chloride gas mixtures by bubbling it through two wash columns containing water or hydrochloric acid of appropriate concentration. The columns are kept at constant temperature by circulating water at the desired temperature. The required water or hydrogen chloride partial vapor pressures were obtained by regulating the temperature of the circulating water. The corresponding partial vapor pressures were taken from the International Critical Tables (19).

Techniques

Preparation of Experiment

An ampoule containing about 100g. of dry melt (Anderson Physics Laboratory)

is hung over the crucible and the furnace temperature is slowly raised to 450°C. Argon gas is passed through the reactor during the melting process. When the salt in the ampoule is completely molten, the tip of the ampoule is broken and the liquid transferred to the crucible, applying slight suction when necessary. Electrodes and gas tubes are inserted on the reactor top and let to dry under vacuum. Special care is taken to prevent thermal shocks to the ceramic or pyrex tubes, by slow equilibration of the temperature. After the electrodes are immersed in the melt, the reactor is evacuated for a few minutes and then flushed with argon. All the experiments are run with argon gas flowing above the melt.

Oxide ions are added to the melt using a fine platinum scoop by adding weighed amounts of dry CaO previously fired for 1 h. at 950°C. The weight of the CaO in the scoop is determined by weight difference of the crucible. The sample weight is corrected for impurities in the CaO by acid titrations of the stock CaO powder. Usually the CaO content of the original powder was around 94 ^{wt}% (Mallinckrodt).

Preparation of Solid Solutions

A quantity of melt is transferred to the crucible and to that, weighed amounts of dry salts are added. The solution is stirred to dissolve the salt, and portions of the molten homogeneous solution are transferred into pyrex tubes of desired inner diameter by applying gentle suction.

The salt in the tubes is let to solidify and the tube is sealed at its two extremities. To perform an experiment, portions of solid solutions are introduced into a new melt to obtain the desired concentration.

The Ni/NiCl₂- Reference Electrode

A few sticks of NiCl₂ solution in KCl-LiCl are introduced into a 60 cm long,

1/4" O.D. standard wall pyrex tube. A 0.5 mm Ni wire whose one end is in contact with the stick and the other end is spot welded to a piece of platinum wire is placed into the tube. After flushing the tube with argon, the platinum wire is sealed to the pyrex glass to provide electrical contact and also obtain a sealed electrode.

The Pt/PtCl₂ Reference Electrode

A constant current of a few milliamperes is passed between a platinum foil electrode of large surface area and a graphite counter electrode, both kept in separate glass-frit or pure alumina compartments. From the charge passed and subsequent analysis of the chloride content in the platinum compartment, the Pt²⁺ concentration is calculated.

The Ni/NiCl₂ - BiOCl - Zirconia Membrane Electrode

A few sticks of BiOCl saturated melt are placed at the bottom of a stabilized zirconia tube, and a Ni/NiCl₂ reference electrode is inserted. The electrode is ready for use after melting of the sticks and temperature equilibration.

Oxygen Gas Reference Zirconia Membrane Electrodes

A thin and porous gold coating is applied on the inner walls of a zirconia tube to about 1/2" from the bottom. To make the coating, Gold, type 100 cermet paste is used (Transene Co.). The tube is filled to about 5 mm height with a few grains of gold or platinum sponge. A gold or platinum foil spot-welded to a nickel wire provides further catalytic area and electrical contact to the measuring instrument. The nickel wire is isolated from the zirconia tube by placing it into a non-porous alumina tube (Degussit, Al-24). This tube also serves as a reference gas inlet to the electrode. Pure oxygen, oxygen-nitrogen mixtures or air are used as reference gas.

A technical problem which has not been satisfactorily solved is the sealing

of ceramic tubes to pyrex or other materials. Such sealing procedures were needed to add to the electrodes the length required by the size of the reactor. All the techniques of sealing which were tried, failed to produce a satisfactory hermetic connection between the tubes. Application of ceramic sealant (Aremco, ultra bond 552) or fusing the tubes by flame invariably failed, because of differences in the thermal expansion coefficients of the materials. Apparently, this is a problem encountered also by others, as failure to achieve vacuum tight seals have been reported in the literature (20). An imperfect solution was however found in this laboratory by either using ultra torr unions (Cajon) with teflon O-rings, or Swagelok unions with Vespel ferrules (All Tech. Associates). The temperatures around the connections being near 400°C, the teflon O-rings and the Vespel ferrules completely disintegrated at the completion of the experiment. Also the metal parts deteriorated, especially when running experiments in the presence of moisture or hydrogen chloride or their mixtures.

Results

Resistance of Zirconia Based Ceramics

CaO and Y_2O_3 stabilized zirconia tubes were first soaked in concentrated hydrochloric acid for two days to remove impurities and were then washed and dried at 150°C in a drying oven.

59m/o LiCl-41 m/o KCl eutectic was prepared by mixing A. R. grade salts and drying the mixture in a vacuum desiccator. Portions of this mixture were weighed into a platinum crucible and in the sample tube in such amounts that when melted the liquid level within the tube will be about 4 cm higher than the level in the platinum crucible. Both the tube and the crucible were placed

in the molten salt reactor and further dried in vacuum (ca. 0.1 mm Hg) at 200°C for 20 hours. After drying, the temperature was raised to above 350°C to let the salt melt.

The conductance between the two sides of the tube and its variation with time was measured with a Wayne-Kerr B221A universal bridge connected to platinum wires immersed into the melt on each side of the tube. As the melt has a resistance of a few ohms only, any resistance measured in the system is attributed to the resistance of the zirconia tube. A constant resistance with time is an indication of the imperviousness of the tube to the melt, while a resistance decreasing with time indicates penetration of melt into the tube.

After a constant value of conductance with time was reached, the effect of source bridge frequency on the conductance was determined between 1000 and 10,000 Hz. A slight decrease of conductance with increasing frequency was found. The results below were obtained from measurements made at 2000 Hz.

The measured resistances can be roughly compared to resistances calculated from data reported in the literature. Dixon et. al. (21) measured the resistivities in air of zirconia tubes stabilized with various amounts of CaO or Y_2O_3 . From the measurements made in the temperature range of 600 to 1200°C on samples having CaO or Y_2O_3 concentrations as near as possible to those of our samples, we derived the following equations for the dependence of the resistivity on temperature:

Stabilizer	Stabilizer Concn.		Derived Equation for ρ , ohms.cm.
	w/o	m/o	
CaO	7 1/2	15.12	$\log \rho = -3.45 + \frac{6.56 \times 10^3}{T^\circ K}$
Y_2O_3	8	4.53	$*\log \rho = -2.51 + \frac{4.34 \times 10^3}{T^\circ K}$

*from 7 m/o Y_2O_3 curve.

Table I

Comparison of Calculated and Measured Resistance of Y_2O_3 or CaO
Stabilized Zirconia Tubes at 450°C.

Description of Tube	Calculated(450°C)*		Measured resistance** in Melt	
	Resistivity, in Air,ohm.cm.	Resistance, in Air,ohms	Initial, ohms	Final,ohms
Exper B, CaO-stabilized Zirconia modified for improved cyclability	4.8×10^5	11,100	5400 (1)	130 (70)
0921, 7 1/2 w/o CaO-stabil- zed Zirconia	4.18×10^5	11,100	620 (0.8)	530 (45)
1372A, 8 w/o Y_2O_3 Stabilized Zirconia	3.13×10^3	80	28 (2.5)	28 (21)

* From Ref. 21

** Figures in parenthesis denote time elapsed in hours since the melting of the eutectic.

In Table I we compare the calculated resistances in air with those measured in the melt. In Fig. 1 the dependence of the resistivity of a yttria stabilized zirconia tube on temperature is shown for the measurements in our melt and compared to Dixon's values taken in air (21).

From comparison of data in Table I it can be seen that the Y_2O_3 stabilized tube has a resistance constant with time and a value comparable to the resistance measured in air. For the CaO-stabilized tubes, the measured resistances are much lower than those calculated and in the case of Exper B tube a great decrease is noted with time. It is evident that the melt is rapidly penetrating into the CaO-stabilized tubes, while the Y_2O_3 tube seems to be impervious.

The effect of temperature on the resistance of Exper B, 7 1/2 w/o CaO-stabilized zirconia tube was also measured. The resistance at 350°C was 5400 ohms and decreased gradually to 430 ohms at 450°C. From these measurements, a linear log R vs. 1/T plot was made, but its validity is doubtful as the data are strongly dependent on time because of the penetration of melt.

Resistance to Thermal Shocks and Chemical Attack

CaO-stabilized Zirconia

These tubes become brittle and crack after a few hours of contact with the melt. Their surface darkens showing an irreversible change in their structure.

Y_2O_3 -stabilized Zirconia

No cracks or fissures are observed in 8 w/o Y_2O_3 stabilized zirconia even after repeated use. Their appearance does not change during or after the experiments, except for a color change from yellow to light orange due to change in temperature. The original color is restored when the tube is brought back to room temperature.

With reasonable care in avoiding thermal shocks, these tubes can be used repeatedly for as long as 500 hours without any damage being observed.

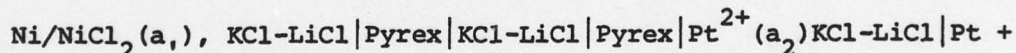
The 16.9 wo/o Y_2O_3 stabilized zirconia tube could not resist even a single soaking in the melt after which it was found cracked at the bottom. It was attacked by the melt as strongly as the CaO-stabilized tube was. Consequently, the CaO stabilized and 16.9 wo/o stabilized zirconia tubes were rejected.

7.5 wo/o Y_2O_3 Stabilized Thoria

The performance of these tubes is similar to that of 8 wo/o Y_2O_3 stabilized zirconia with respect to resistance to thermal shocks and chemical attack. However, they are extremely fragile and will crack under the slightest mechanical stress. Their electrochemical behavior is similar to that of 8 wo/o stabilized zirconia.

The Standard Potential of Ni/NiCl₂ Reference Electrodes

The potentials of the Ni/NiCl₂ electrodes were measured in the following cell:



From these measurements, first the potentials against 1 M Pt^{2+} reference were computed:

$$E_{Ni/NiCl_2} = E^\circ_{Ni/NiCl_2} + \frac{0.1434}{2} \log a_2 = E^\circ - 0.129 \text{ v } (a_2 = 1.61 \times 10^{-2} \text{ M})$$

The standard potential (for 1 M NiCl₂) of the electrodes were calculated using this value and the actual concentration of Ni^{2+} in the electrode:

$$E_{Ni/Ni^{2+}} = E^\circ_{Ni/Ni^{2+}} + \frac{0.1434}{2} \log a_1$$

$$E^\circ_{Ni/Ni^{2+}} = E_{Ni/Ni^{2+}} + 8.17 \times 10^{-2} (a_1 = 7.25 \times 10^{-2} \text{ M})$$

The results obtained are summarized in Table II.

Table II

Standard Potentials (E°_M) and Resistances (R) of Ni/NiCl₂ Reference
Electrodes at 450°C in LiCl-KCl Eutectic Melts.

Electrode No.	E, Measured, V, vs Pt/Pt ²⁺ (a)	E°, V. vs 1M Pt/Pt ²⁺	E° $\frac{M}{V}$,	R Ohms
M4N8 pure Ni wire end				
1	-0.7433	-0.8719	-0.7902	17600
2	-0.7437	-0.8723	-0.7906	10000
3	-0.7444	-0.8730	-0.7913	12800
4	-0.7446	-0.8732	-0.7915	12300
Ordinary Ni wire, unknown purity				
5			-0.7878	
6			-0.7944	
7			-0.7937	
8			-0.7907	

(a) $a_{\text{NiCl}_2} = 7.25 \times 10^{-2} \text{ M}$; $a_{\text{Pt}^{2+}} = 1.61 \times 10^{-2} \text{ M}$

The average values for the two sets of electrodes are:

-791.0 \pm 0.5 mv for the first set and

-792 \pm 2 mv for the second.

The difference between the two sets is 1 only mv.

These values which differ no more than a few millivolts from each other, should be compared with $E_M^\circ = -0.795$ V reported by Laitinen and Liu (22) for Ni/NiCl₂ without pyrex glass walls. The resistances of the electrodes are around 10 to 17 kohms at 450°C, low enough to enable measurements of the potential with potentiometers not requiring high input impedance.

Although these electrodes are easy to make, the pyrex glass walls deteriorate too soon by contact with the melt, especially in the presence of oxide ions. Their use in experiments involving oxide ions is not recommended, as is also known that glass consumes oxide ions (23).

The Nernstian Response of Zirconia Membrane Electrodes to Changes in Oxide Ion Concentration in Melts.

The experiments were carried out using two types of oxide references in a 8 wo/o Y₂O₃ stabilized zirconia tube:

-a Ni/NiCl₂ reference electrode in contact with a solution of CaO or a saturated solution of BiOCl in the KCl.LiCl melt;

-O₂, air or O₂/N₂ mixtures flowing inside the tube with the gas contacting a catalytic surface of platinum or gold.

This type of reference was also tested with a 7.5 wo/o Y₂O₃ stabilized thoria tube (furnished by Dr. Bauerle from Westinghouse).

The Ni/NiCl₂-Oxide Reference

The response of the electrode to changes in oxide ion activity in the melt were measured in a cell of the type:

+Ni|NiCl₂(KCl.LiCl)|CaO(a),KCl.LiCl|Z|CaO(a_x)KCl.LiCl|NiCl₂(KCl.LiCl)|Ni -
where Z represents the zirconia membrane.

The advantage of using such a cell lies in the similarity of potentials of the two Ni/NiCl₂ reference electrode (except for a small liquid junction

potential). Such an arrangement permits the direct measurement of the ratio

$a_{\text{CaO}}/a_{\text{O}^{2-}}$ from:

$$E = \frac{RT}{2F} \ln \frac{a_{\text{CaO}}}{a_{\text{O}^{2-}}} \quad (130)$$

A good linear plot is obtained, as shown in Fig. 2, with a least squares fit for a slope of 67 mv. compared to 71 mv expected at 450°C. However, the individual data points fall on a somewhat higher line, indicating the presence of an oxide like interference in the experiments.

The rate at which equilibrium potentials are attained is rather slow. More than 12 hours of contact with the melt are needed to obtain reasonably steady potential values.

In a similar experiment, melt saturated with BiOCl was substituted for the CaO solution in the zirconia reference compartment. By using BiOCl as reference oxide, the O^{2-} concentration was reduced and was kept constant ($S_{\text{BiOCl}} = 6.6 \times 10^{-4} \text{ M}$ (2)). In this way, it was thought that lower concentrations of unknown oxide could be determined, but it was found that, the lower limit of detection was set by the efficiency of the Argon purification line and the leak-rate of air entering the reactor and not by the oxide concentration in the reference compartment.

To make the measurements in very pure melts, the residual oxide or hydroxide present was first removed by flushing the melt with hydrogen chloride gas, and removing the excess hydrogen chloride with dry argon. During these treatments great changes were observed in the membrane e.m.f. with HCl bubbling. The potential difference at the two sides of the membrane became as low as -400 mv. (outer electrode at input). Assuming the saturation concentration of BiOCl to be $6.6 \times 10^{-4} \text{ M}$ (2) it can be estimated that the oxide concentration in the melt remaining after the HCl treatment is around 10^{-9} M , from the equation:

$$-400 = 71.7 \log \frac{(a_{\text{O}}) \times}{6.6 \times 10^{-4}}$$

The potential of the cell could be raised by flushing with argon or by evacuation, the electrode responding rapidly to these potential changes. For example, in a hydrogen chloride admission cycle the changes observed were as follows:

Original potential:	+44 mv.
Bubble HCl, ΔE gas down to:	-400 mv.
Flush with argon, ΔE goes up to:	+16 mv.

After reaching a stable potential under argon, a slow change of potential at a rate of 2 to 5 mv.per hour is observed. Apparently, this change is due to the consumption of oxide from the melt by the pyrex walls of the Ni/NiCl₂ electrodes. In fact, until an experiment is completed, the reference electrode is in continuous contact with the oxide containing melt for about 200 hours. During this time, the pyrex wall often becomes very strongly etched, while that in contact with the reference solution ($6.6 \times 10^{-4} \text{ M}$) remains practically unattacked.

The final potential reached by the membrane changes also with the total pressure above the melt. In one typical case, the potential rose from +40 to +65 mv. by evacuating the reactor with a rotary pump (about 0.01 mm Hg pressure) and dropped to +21 mv when argon was readmitted. The introduction of an ascarite column to the argon purification line did not change the behavior of the electrode, indicating that the change of potential with pressure is not due to the presence of carbon dioxide in the surrounding atmosphere. However, admitting air to the reactor causes the potential to rise sharply showing that the electrode is rapidly responding to the partial pressure of oxygen and/or moisture in the air. The effect of oxygen and water partial pressures could

not be determined separately, as, in the experimental set up, the reference and the unknown oxide solution were surrounded by the same atmosphere.

The Nernstian response of a new zirconia tube stabilized with 8 wo/o yttria was measured, against melt saturated with BiOCl serving as reference solution. The experimental curve best fitted the equation:

$$E_{\text{exp, mv.}} = + 249.1 + 61.4 \log (a_{\text{O}} =)_x \quad (14)$$

in the range 10^{-4} to 10^{-2} M oxide, compared with the theoretical equation based on K_{sp} (2) of BiOCl and the value of $RT/2F$ at 450°C .

$$E_{\text{calc, mv.}} = + 243.6 + 71.7 \log (a_{\text{O}} =)_x \quad (15)$$

The Gas Reference Electrode

A schematic drawing of the gas reference electrode is shown in Fig. 2. The solid electrolyte tube can be either 8 wo/o Y_2O_3 stabilized zirconia or thoria. The inflowing gas is either pure oxygen, or its mixtures with nitrogen or air. Where air is used, the electrode tip is left open to contact with the surrounding atmosphere. Various ways of joining the solid electrolyte tube to pyrex tubing were tested, including the use of high temperature sealers and mechanical connections. Finally, the Cajon ultra-torr union with teflon o-rings was adopted. The slope of the potential of a $\text{Y}_2\text{O}_3 - \text{ZrO}_2$ electrode measured against a Ni/NiCl_2 reference electrode, vs $\log C_{\text{O}}$ at 400°C was 68 mv per decade with pure oxygen flowing in the electrode. The theoretical value was 67 mv within the concentration range of 10^{-4} to 10^{-2} M CaO in the melt.

It was found that the response of the electrode to concentration changes was very slow requiring, in most cases, overnight stabilization. It was suspected that the slow step in the measurement involved the Ni/NiCl_2 electrode.

In fact, when two identical O_2 electrodes, differing only in PO_2 value, were immersed in an oxide ion containing melt, equilibrium values were reached in a few hours, compared to 16 to 20 hours needed using the $Ni/NiCl_2$ reference electrode. It was also found that the slope for the $\log PO_2$ vs ΔE curve using two oxygen electrodes with differing PO_2 , was only 50 mv per decade; much lower than the 67 mv expected. The reasons for this discrepancy may be due to lack of catalytic activity in the $O_2 \rightleftharpoons 2 \text{electrons} + 1/2 O^{2-}$ reaction.

In a similar experiment a 7.5 wt% Y_2O_3 stabilized thoria tube was used as solid electrolyte. The solid electrolyte to pyrex tube connection was made with swagelok with vespel ferrules (All-Tech), but because of lack of availability, brass connections instead of stainless steel were used which, inevitably deteriorated in a short time. Also, the Vespel ferrules were found to be carbonized in spite of their alleged resistance to heat in the present chemical environment. The temperature near the ferrules was not above $350^\circ C$.

Because of strong leaks in the thoria to pyrex connections, quantitative data could not be collected in this experiment, but the following observations help summarize the behavior of thoria:

-generally the thoria electrolyte behaves similarly to zirconia concerning the Nernstian response and the rate of attainment of steady potentials.

-both electrodes are sensitive to the composition of the atmosphere above the melt, but this may not be a conclusive statement, as continuous leaks at the unions may affect the results. Nevertheless, it was observed that, admitting a few bubbles of moisturized argon or pure oxygen caused an increase in potential, in the same direction as would be expected by a decrease in oxide concentration.

Discussion

Because of the unique mechanism of oxide ion transport in stabilized ceramic membranes, it may be assumed a priori that when used in concentration cells as solid electrolytes, these membranes will behave as specific ion electrodes with respect to oxide ions. Due to their electronic configuration which is different from that of $O^{=}$ ion, other species of oxygen (water, hydroxide, peroxide and super-oxide) cannot possibly penetrate the membrane.

In spite of this specificity, the electrode may respond in an indirect manner to the presence of these ions as far as they take part in reactions involving the consumption or production of oxide ions:

Reactions with Water

In the presence of water, oxide produces hydroxyl ions:



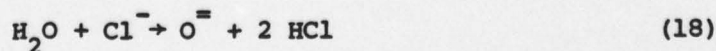
Lysy and Combes (8) were able to measure an equilibrium constant for the above reaction:

$$K_1 = \frac{x_O^{=} \cdot P_{H_2O}}{x_{OH^{-}}^2} = 0.18 \text{ at } 727^{\circ}C \text{ (X = mole fraction)} \quad (17)$$

in KCl-LiCl melts. The equilibrium constant was obtained from e.m.f. measurement with a CaO stabilized zirconia electrode, at various partial pressures of water in the presence of a constant initial concentration of OH^{-} ions. No mention was made of the rate of attainment of equilibrium.

Reactions in Acid Solutions

In moist acidic melts, water behaves as a base producing oxide ions:



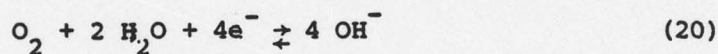
The same authors (8) obtained the value of $10^{-7.74}$ at $727^{\circ}C$ for the equilibrium constant:

$$K_2 = \frac{x_O \cdot P_{HCl}^2}{P_{H_2O}} \quad (19)$$

showing that hydrogen chloride reacts quantitatively with oxide. The steep and rapid decrease of the potential of our zirconia electrode when hydrogen chloride gas was introduced into the melt also confirms the fast and quantitative nature of the reaction, reminiscent of strong acid-base reactions in aqueous systems.

Reactions of Oxygen and Water

Under potentiometric conditions and in moist melts, oxygen impurity in the cover gas can react with water in the melt to give hydroxyl ions:



The hydroxyl ions can dissociate to produce oxide:



Considering our experimental conditions, it may be possible that our melts contained always these impurities, for these reactions to occur even at very low concentration levels. This may explain the changes observed in the zirconia electrode potentials with changes in the gas composition above the melt.

Plan for Future Work

In continuation of the present research the following steps will be followed:

-Technical improvements of the electrode: it is necessary to either devise a reactor geometry where short zirconia tubes can be used (about 6" long) or to develop a proven way to seal heremetically zirconia to pyrex.

-The reason for the dependence of the electrode potential of the composition of the atmosphere must be carefully investigated to see whether the effect is real or spurious.

-A version of the oxide sensor electrode will be investigated in which a thincoating of stabilized zirconia will be applied to a semi-porous matrix like alumina. The zirconia side will be exposed to oxide containing melts, while the alumina side will serve as the reference oxide (or oxygen) compartment. By regulating the thickness of the zirconia coating, the rate of transport of oxide ions within the membrane can be controlled and measured.

-After a reliable electrode is developed, its specificity, and its time of response with respect to changes in oxide ion concentrations will be tested. For specifity studies, experiments will be made in the presence of H_2O , OH^- , O_2^- , $\text{O}_2^{=}$ and H^+ ions.

-A reliable electrode will enable the derivation of chemical data pertinent to basic research in molten salts, like acid-base equilibria constants, activity products of oxides, and rates of reactions involving oxide ions in melts.

Summary

Zirconia based solid electrolytes of various compositions have been tested as membranes for electrodes specific to oxide ions. Among those tested, 8 wo/o Y_2O_3 -stabilized zirconia proved to be the best electrolyte that can be used to this end. It is extremely stable in the melt and resistant to thermal shocks and chemical attack. Zirconia stabilized with 16.9 wo/o Y_2O_3 or 7 1/2 wo/o CaO is not thermally or chemically resistant. 8 wo/o Y_2O_3 stabilized thoria behaves in a manner similar to 8 wo/o Y_2O_3 stabilized zirconia, but its use is not recommended because of its extremely high cost (\$400 for a 6" x 1/4" diam. tube.)

The 8 wo/o Y_2O_3 stabilized zirconia responds almost as theoretically expected to changes in oxide ion activities in melts.

As a secondary objective, various kinds of reference electrodes were developed which are easy to prepare and use.

Although this research is still in laboratory stage, the results obtained so far indicate that a practical and reliable electrode can be built following the lines developed in this project.

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Fig. 1

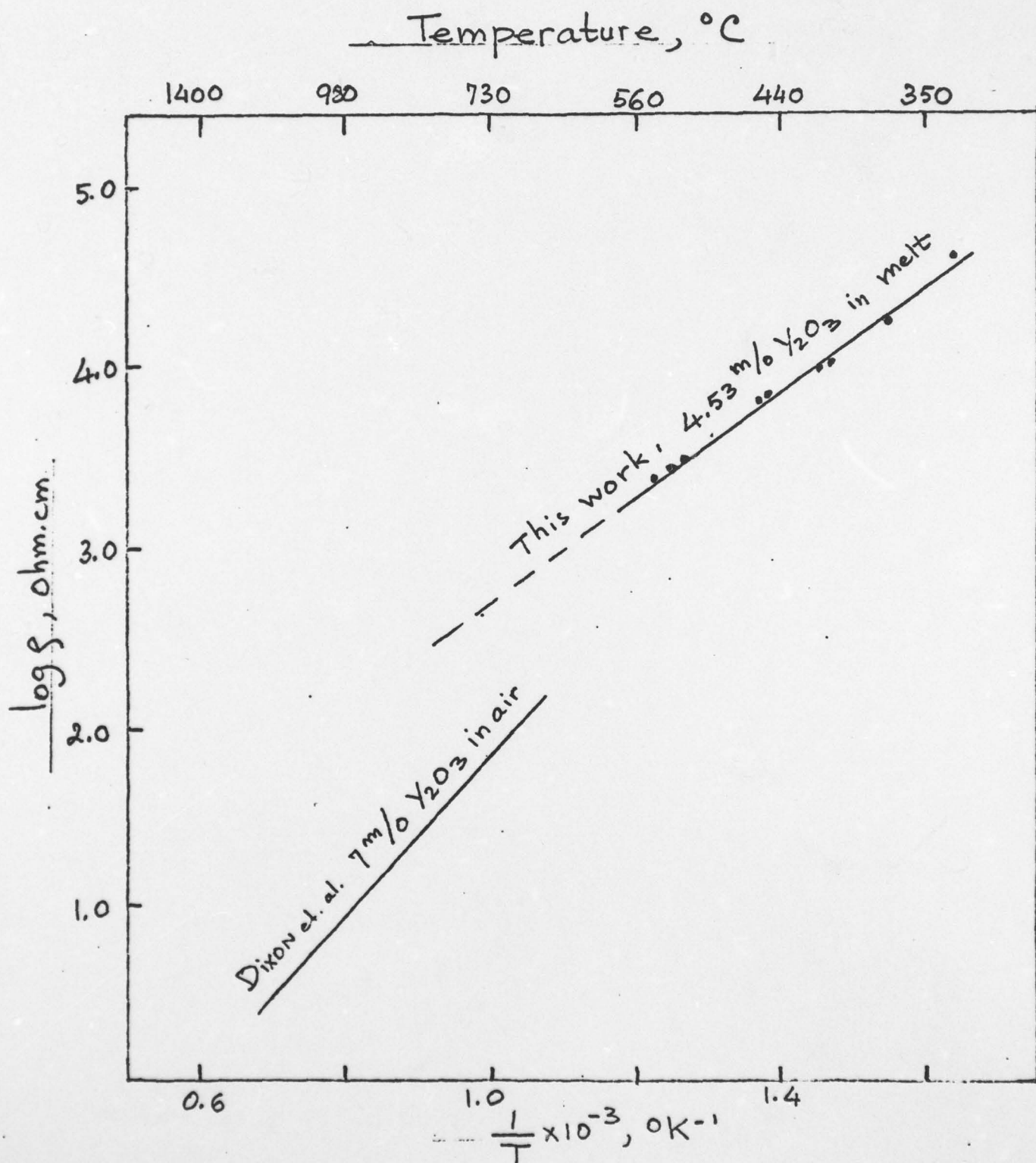


Fig. 2

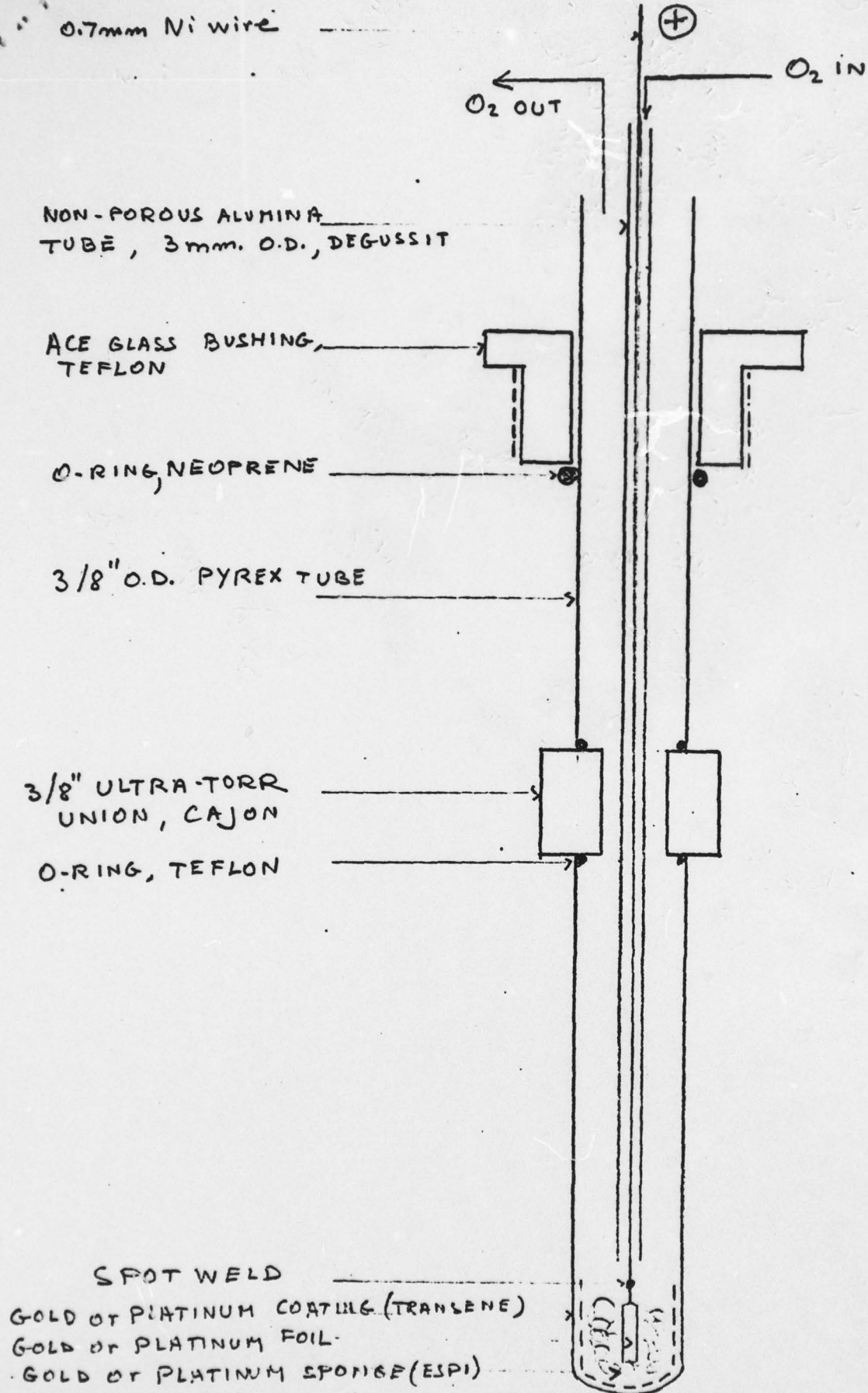


Figure Legends

Fig. 1 Dependence of resistivity on temperature for 4.53 m/o Y_2O_3 stabilized zirconia in KCl-LiCl melt. Wall thickness 1/16" exposed surface area: 9.93 cm^2 and comparison with measurements in air (ref. 21).

Fig. 2 Configuration of the oxygen gas reference electrode.